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Surface Engineering for Molecular Electronics

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INTRODUCTION

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Molecular electronics studies charge transport through molecules and the applications in electronic devices comprising these molecules as building blocks. The field of molecular electronics began with the innovative measurements of electronic conductivity through monolayers of cadmium salts of fatty acids by Mann and Kuhn in 1971.[1] They observed an exponential decrease of conductivity with increasing thickness of the monolayers, which revealed electron tunneling through the organic monolayers. Later in 1974, Aviram and Ratner theoretically proposed that a molecule comprising donor and acceptor moieties could manifest asymmetric charge transport.[2] Their work provided an *ad hoc* approach to predict the charge transport through molecules, which set the step-stone for many following studies that eventually united through the development of the non-equilibrium Green's functions.[3–5] It was apparent that a single molecule or the ensemble of molecules could be fabricated into electronic devices, such as resistors or diodes, by forming a circuit with two electrodes. However, the realization of such circuitry remained one of the challenges at that time for molecular electronics.

The invention and development of scanning tunneling microscopy (STM) and atomic force microscopy (AFM) in the 1980s hugely propelled the field of molecular electronics for they provided conventional platforms to measure the conductance of a single molecule and ensemble of molecules. Simple σ -bonded systems (*e.g.*, alkanes) and aromatic systems (*e.g.*, benzene) functionalized by thiols were kinetically trapped as a single molecule between two electrodes or contacted by a conductive tip in a densely-packed monolayer, allowing the measurements of currents under applied biases.[6–9] These pioneering studies advanced the methodology for determining the electrical conductivity of different molecules and provided insights into their charge transport properties from a well-defined approach. The large fluctuations in the experimental data and the characterization of the molecules in the junctions, whether as a single molecule or ensemble, still remained challenges at the time. But the success of the early experiments, the advantage of molecule electronics in creating devices within the scale of a molecule and the tunable charge transport properties over rational synthesis, have raised broad interest around the world and led to fruitful discoveries over the past 40 years.

1.1. LARGE-AREA AND SINGLE-MOLECULE JUNCTIONS

There are two major experimental approaches to molecular electronics, one based on single-molecule junctions[10–12] and the other based on large-area junctions comprising monolayers or ensembles of molecules[13–18]. Both approaches flourish and are complementary to each other in the field of molecular electronics but large-area junctions show more promise for practical applications.[19] Despite their difference in dimensions, the separation between two electrodes in both junctions is usually the length of a molecule, even with molecular wires[20, 21] and electrochemically-grafted thin films[18, 22]. Notably, monolayer-based transistors that exploit the in-plane electrical conductivity of monolayers in the configuration of field-effect transistor (FET) are an exceptional, but are functionally much more similar to the devices based on inorganic materials.[23–25] Putting that exception aside, charge transport across large-area junctions can be approximated to a superposition of numerous, parallel events in single-molecule junctions.[26] However, the generalization among these approaches is still unclear, *e.g.*, whether the

wave function of the electron is constrained to each individual molecule or delocalized in large-area junctions in comparison to its counterpart. In single-molecule junctions, it is obvious that the physical and chemical nature of the molecules (*e.g.*, the molecular lengths and molecular orbitals) that dominate the charge transport properties emerge from quantum mechanical phenomena, *e.g.*, tunneling. Such approaches mitigate the effects that arise from interacting with neighboring molecules and monitor the occurrence of electrical events by kinetically trapping individual molecules between the electrodes. Hence the observation of charge transport across single-molecule junctions is also affected by the vibration of molecules and averaged over time to yield the actual properties, in contrast to that of large-area junctions where the observation is spatially averaged over a layer of (well-defined densely-packed) molecules. Large-area junctions, on the other hand, allow investigations into macroscopic, collective effects that emerge from molecules interacting with their surroundings in monolayers. Physical properties such as dielectric constant and capacitance, which are difficult to characterize in single-molecule junctions (*e.g.*, the capacitance cannot be unambiguously partitioned from charge rearrangement within the electrodes as a result of dipole-induced dielectric response and the polarization of the molecules), can be better studied in a controlled manner in monolayers. Intermolecular interactions in monolayers and through-metal interactions between molecules and electrodes facilitate lateral coupling of energy levels and charge transport across large-area junctions.[27] The electric field of an isolated molecule decreases less significantly with increasing distance to the molecule, compared to that of a monolayer of identical molecules in which the cancellation of the lateral electrostatic components converges the electric field into a constant from a closer distance.[28, 29] Hence in large-area junctions, the charge migration from the molecules to the substrate has minor influence on the electrostatic phenomena because the electric field is suppressed outside the monolayers. Instead, the intermolecular dipole-dipole interactions partially depolarize the molecules (dipole reduction) and dominate the electrostatics in the monolayers.[29] On the other hand, charge migration between the molecules and the substrate plays a major role in the electrostatics of single-molecule junctions. This significant difference allows monolayers to modify energy levels at the interface more effectively than single molecules.

The emergence of collective effects is also related to the lateral dimensions of the molecular junction. The charge transport properties between a single-molecule junction and a 1000nm^2 large-area junction of the same molecule can be vastly different.[30] But such difference is remarkably smaller between a 50nm^2 junction and a $1000\mu\text{m}^2$ junction.[31, 32] Because the intermolecular distance of the ensemble in large-area junctions is often lower than 1nm , a 50nm^2 junction then comprises the several hundred densely-packed molecules that are sufficient for collective effects. On such basis, further increasing the junction size for devices compatible with photolithography and microfluidics should not affect the charge transport properties across the junctions.[33–37] In practice, junctions with larger size are more susceptible to defects and irregularities from the ensembles and substrates that play a major role to short circuits and undermine the performance of the junctions.

The difference between the single-molecule approach and the large-area approach is pronounced in their statistical nature. The measured current that traverse a single-molecule junction is totally stochastic due to the soft nature of the molecules that are

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kinetically trapped between the electrodes. Large-area junctions, on the contrary, are expected to produce current as a sum of myriad charge transport events across the monolayers simultaneously. Hence the charge transport properties characterized on individual large-area junctions are directly comparable and more reproducible than that from single-molecule junctions, with significantly fewer measurements (typically within 100 junctions compared to over thousands of junctions in single-molecule approach) required for the characterization.[14, 38] One might argue that the resulting charge transport properties across large-area junctions differ on the model selected for data analysis and the type of junctions[39, 40], but the same argument also holds for single-molecule junctions. Notably, the measured current in large-area junctions is dependent on the effective contact area, contact mechanics and even defects that give rise to high conductance[41, 42], while the collection of currents in single-molecule junctions allows interpretation on various charge transport scenarios, even identifying charge transport pathways through the molecules[10, 43, 44]. Large-area junctions offer higher sensitivity than single-molecule junctions in characterizing less conductive molecules, in the sense that the current per molecule in large-area junctions can be mathematically extracted from the measurable current over contact area and thus mitigates the limitation of equipment sensitivity. Hence it is commonly perceived that the large-area approach is better than single-molecule approach for characterizing the charge transport properties of long molecules, in which the conductance decays exponentially over increased molecular length. In junctions where the metallic states (or Fermi levels) of the electrodes extend into the molecules, it is necessary to decouple the intrinsic properties of the molecules from the hybridization of molecular orbitals with the electrodes by measuring longer molecules and the advantageous large-area junctions are useful for such applications.[45–47]

In the vast majority of studies, single-molecule junctions are formed and characterized in a non-equilibrium state. In the conventional STM break junctions and mechanically controlled break junctions techniques, the metallic electrodes as well as the junctions form and break repeatedly and dynamically. In single-molecule junctions formed using electromigration breakdown technique, nanogaps are obtained by breaking nanowires upon aggressive heating and bridged by molecules, which brings enormous challenges to the control over gap size and the reproducibility of the devices.[48] Researchers have tried to use reactive graphene edges and covalently-bound fullerene dumbbells to form single-molecule junctions, however the structure of the junctions is not well characterized and the utilization of this approach is limited by the challenging synthesis of desired molecules.[49] Moreover, single-molecule junctions in most scenarios require weak molecule-electrode interactions so that a single molecule can diffuse in between the electrodes upon their formation.[50] In the break junction technique, the examined molecules are constantly mechanically stretched[44] or compressed [42, 51–55] by the electrodes and the impact of molecular deformation on the charge transport properties of the molecules may be overlooked in single-molecule junctions. On the contrary, the configuration of molecules present in large-area junctions can be determined and efficiently modified over interactions at the interfaces (e.g. molecule/electrode interfaces and molecule/molecule interfaces). It is obvious that the stable, well-defined character of large-area junctions is more promising for practical applications than single-molecule junctions. Alkanedithiols have shown reproducible conductivity that follows an exponential decay over molecular

length in large-area junctions and serve as a standard reference[17]. However this trend can only be poorly reproduced in single-molecule junctions with an immensely broad data distribution[56] or multiple conductance states that correspond to different binding modes between the molecules and the electrodes[44].

In general, the applicable complementary characterizations of single-molecule junctions and large-area junctions are drastically different because of the nature of the junctions. The monolayers in large-area junctions are already in their equilibrium state and compatible with a large variety of surface spectroscopy that inspects over μm^2 - mm^2 area, thus their qualities can be plainly perceived and controlled.[48, 57–62] On the contrary, the states of the molecules trapped between electrodes in single-molecule junctions cannot be directly investigated and the determination of the presence of a molecule often relies on internal references, for example, the conductance of a quantum point contact of the electrodes is used to tell apart the plateau that corresponds to charge transport through a molecule in break junction technique.[45] High-order differentiation by inelastic electron tunneling spectroscopy (IETS), noise analysis and employing external field, *e.g.*, electric field (electric gating) or thermal gradient are useful to gain additional insights into single-molecule junctions. These tools are not compatible for large-area junctions in most scenarios due to their geometrical limitations (*e.g.*, the fabrication of gate electrodes). Exceptionally, *in situ* spectroscopy with photoactivation[63–65] and IETS[66, 67] are feasible tools for complementary characterizations of large-area junctions.

In summary, single-molecule junctions and large-area junctions are two complementary approaches in the field of molecular electronics. Though designed to tackle specific and different challenges, they both serve as media to convey knowledge that deepens our understanding of the underlying physics of charge transport through molecules and helps to convert those properties into practical devices. Large-area junctions specifically examine molecules as ensembles in their equilibrium state, which is a desirable feature ensuring reliable device performance. The structures of the molecular ensembles in large-area junctions, apart from the molecules themselves, can be chemically modified to affect the function (charge transport properties) of the junctions. Because of these compelling features, we chose to dive into large-area junctions in this dissertation. In the following section, we will survey the molecular monolayers for large-area junctions.

1.2. MOLECULAR MONOLAYERS

The interface between the molecular monolayers and the electrodes plays a crucial role in controlling the charge transport properties of large-area junctions. Rich studies on the formation and properties of molecular monolayers can be found in literature[68–74], and they have found applications across many scientific and engineering disciplines, *e.g.*, anti-fouling surface[75], lubrication[76], corrosion resistance[77], protein binding[78], DNA assemblies[79], cellular signaling and interactions[80], photovoltaics[81] and transistors[82]. Based on the binding strength between the molecules and the electrodes, the process of forming molecular monolayers are categorized into "physisorption" and "chemisorption".[15, 17] The interactions amongst the molecules and between the molecules and the electrodes usually dominate the process of forming molecular monolayer and largely contribute to their structure and stability. Nonspecific adsorption,

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Langmuir trough-based monolayers and self-assembled monolayers (SAMs) are the three common approaches that leverage such interactions to form molecular monolayers.

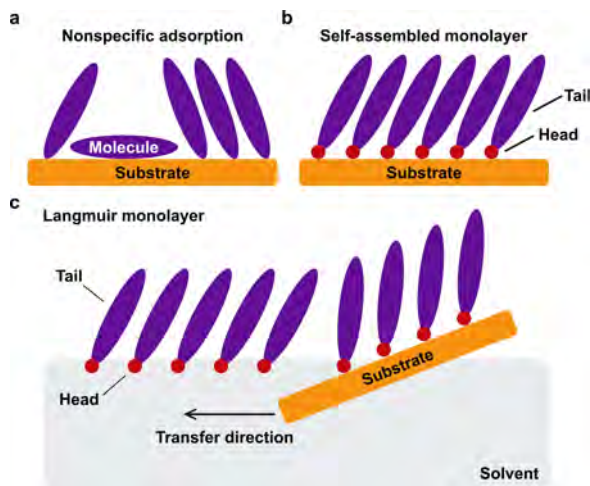


Figure 1.1 | Schematic drawings of the three types of molecular monolayers. **a**, In monolayers formed by nonspecific adsorption, the lack of dominant interaction with the substrate and between molecules may result in the varied orientation of molecules and the formation of multilayer. **b**, The formation of self-assembled monolayers are governed by the reaction between the head group (red) and the substrate, while intermolecular interactions between the tails (purple) facilitate packing of the molecules. **c**, To form Langmuir monolayers, amphiphilic molecules are oriented and packed at the liquid/gas interface and transferred onto a solid substrate.

1.2.1. NONSPECIFIC ADSORPTION

Molecules that do not facilitate specific binding (*e.g.*, lacks specific binding site) with the electrodes can form monolayers via nonspecific adsorption, *e.g.*, monolayers generated from vacuum deposition of the molecules or exposing substrates to a solution of proteins (Fig. 1.1a). While the nonspecific bindings of proteins are mostly undesired for biosensing, nonspecific adsorption is a common approach in molecular electronics to produce monolayers from a large variety of molecules (*e.g.*, fullerenes and pentacenes). However, the formation of monolayers via vacuum deposition is not self-limiting which often leads to multilayers with thickness dependent on dosage and temperature. Moreover, the interaction between the molecules and the substrate has to be stronger than that among the molecules themselves to guarantee uniformity of the monolayers and the prevention of forming islands. The dominant interactions that dictates the orientation of the molecules on the substrates are usually van der Waals interactions, π electron-orbital interactions (especially between conjugated molecules and metallic substrates) and charge exchange.[83] Intermolecular interactions facilitate lateral packing and long-range order of the molecules of which the studies using STM exist in the literature. Nonspecific adsorption, as an approach to fabricate molecular monolayers, still contribute in thin-film organic electronics, surface engineering and molecular electronics.[84, 85]

1.2.2. LANGMUIR TROUGH-BASED MONOLAYERS

The molecules used in the fabrication of Langmuir trough-based monolayers are analogous to the amphiphilic building blocks in the assembly of a cell membrane.[86] The head/tail concept of design was later implemented for self-assembled monolayers. Langmuir monolayers are formed at the liquid/gas or liquid/liquid interfaces and transferred onto solid substrates (Langmuir-Blodgett films based on vertical transfer and Langmuir-Schaeffer films based on horizontal transfer), which distinguishes it from SAMs where the molecules are directly adsorbed onto the substrates (Fig. 1.1c). Hence the major driving force in the formation of Langmuir monolayers is the hydrophobicity/hydrophilicity of the head/tail moieties of the molecules. The choices of head groups for forming Langmuir monolayers are usually polar carboxylic or phosphonic acids, while the tails can be alkyl groups with varied lengths and substitutions that exhibit hydrophobicity. Besides liquid/liquid and liquid/gas interfaces, polar head groups also facilitate formation of monolayers using conventional deposition techniques, *e.g.*, molecules tethered by aggregation and growth ("T-BAG") [87] and spin-casting [88, 89]. In these cases, the polar head groups were repelled from the less polar solvents and facilitate the formation of ordered monolayers at the liquid/solid interface. While some researchers tend to classify these monolayers as a unconventional Langmuir films [90], we argue that the driving force in the process of forming these monolayers is the chemical reaction between the head groups and the substrates, which fall into the category of self-assembled monolayers elaborated in the next section. These methods, however, may pave the way to fabricate Langmuir monolayers without the presence of ionic species (because water is not used) and with enhanced stability (post-formation treatment to form chemical bonds between the molecules and the substrates).

As mentioned earlier in this chapter, the pioneering experiments on molecular electronics were carried out on Langmuir-Blodgett monolayers of adsorbed fatty acids.[1, 91] However, the physical and chemical nature of the Langmuir monolayers (*e.g.*, unstable structures generated from weak bindings between the molecules and substrates, residuals of ionic species and substrate oxidation due to sample preparation) are also the self-limiting factors for this technique to have further practical applications in molecular electronics. On the other hand, the dynamic arrangement of molecules in Langmuir monolayers makes such system a potential candidate for studying the lateral diffusion of molecules, *e.g.*, proteins ("rafting") and phase transitions in the monolayers. As the technique is not restrained to the formation of monolayers (*i.e.*, bilayers can be fabricated), a stable platform that exhibits dynamic molecular arrangement may provide future prospect for Langmuir films.

1.2.3. SELF-ASSEMBLED MONOLAYERS

The self-assembled monolayer is the most extensively studied platform in large-area junctions (Fig. 1.1b). The molecules that are the building blocks for SAMs are functionalized with specific anchoring groups ("head"), *e.g.*, silanes for silicon [92] and thiols for coinage metals [93, 94], which exhibit stronger affinity towards the substrates than the rest of the molecules ("tail"). The driving force in the formation of SAMs is the interactions between the anchoring groups and the substrates, while the choices of tails facilitate

packing via intermolecular interactions, for example, van der Waals interactions from alkyl chains[95, 96], $\pi - \pi$ stacking from conjugated systems[42, 97] (see also in **Chapter 2**), hydrogen bonds[98, 99] and Coulombic repulsion[100, 101]. And depending on the chemical nature of the anchoring groups, the formation of the SAMs can be controlled via temperature, humidity[102], concentration[103], Coulombic repulsion and steric hindrance between charged[59] or bulky anchoring groups[104]. Additionally, the matching between the molecules and the substrate lattice, and the substrate surface lattice forces also contribute to the quality of the SAMs.[95, 97]

Molecules functionalized by anchoring groups on both ends, *e.g.*, dithiols[105] and diamines[106], are often used to facilitate bindings to both electrodes in single-molecule junctions (especially break junctions)[45, 107] in repetitive fashion or to fabricate micro-patterned stationary electrodes in large-area junctions[108–110]. The introduction of multiple anchoring groups can lead to undesired bindings between both anchoring groups to the substrate or the formation of multilayer, which undermines the quality of SAMs.[103, 109, 111, 112]

To ensure the formation of high quality SAMs, we have to consider the choice for substrate and anchoring groups based the purpose of the monolayers. SAMs can be fabricated on hydroxyl-functionalized metal oxides to modify the properties of the dielectric layer in organic field-effect transistors.[113] Although most metal oxides are insulators, atomic layer deposition (ALD) offers controlled fabrication of metal oxide layers with minimal thickness on conductive substrate as part of the bottom electrode that binds phosphonic acid-functionalized molecules in large-area junctions.[114] A more common practice is to grow SAMs on Si-H/Si-Cl terminated silicon surfaces that facilitate the covalent attachment of molecules using an extended arsenal of anchoring groups.[60, 68, 115, 116] The drawbacks of SAMs on semiconductors include the special handling of substrates (removal of oxide layer and preventing further oxidation) and ill-defined electrical conductance, which undermine the development of such SAMs for practical applications. Another major combination is thiols on coinage metals, *e.g.*, Au and Ag. One of the remarkable features of these SAMs is the surface diffusion of thiol-bound metal atoms (for example, thiol bound Au).[50] The similar strength of S-Au bonds compared to that between Au atoms allows thiol-bound Au atoms to diffuse on the surface to reach thermodynamic equilibrium in the packing of the molecules, giving rise to ordered SAMs which is beneficial for stable large-area junctions.[117] Other combinations such as silane and phosphonic acid on hydroxyl-functionalized substrates facilitate the formation of SAMs via condensation reactions.[87] Recently, SAMs formed by leveraging $\pi - \pi$ interactions[118] between aromatic anchoring groups and graphene substrates, bindings between carbenes and Au[119], interactions between fullerenes and coinage metals and dipole-dipole interactions between oligoethylene glycols[104] (see also in **Chapter 4** and **Chapter 5**) provide several alternative routes to fabricate monolayers for large-area junctions.

When introducing functionalities into the SAMs, their stability in large-area junctions should also be considered. For example, SAMs fabricated on rough surfaces are more prone to defects which are responsible for ill-defined conductance or shorts in the junctions.[120] To this extent, the stability of the junctions can benefit from ultra-flat electrodes, *e.g.*, template-stripped metal substrates[121] (cm^2 scale) and Au(111) on

mica (μm^2 scale). Additionally, the stability of SAMs can be further enhanced by post-formation reactions, *e.g.*, metal ligation[122], condensation (to form extra layers)[123] and click chemistry[124]. However, these approaches change the chemical nature the molecules and may significantly alter the electrical properties of SAMs from their original design. Another common strategy is to use mixed monolayers to incorporate functional molecules (for example, bulky photoswitches), that are unable to form high quality SAMs on their own, into inert monolayers.[8, 125–128]

1.3. FABRICATION OF LARGE-AREA JUNCTIONS COMPRISING SAMs

Finding a proper SAM is only half of the production of an ideal large-area junction, the other half of the endeavour is to fabricate a suitable top electrode that preserves the integrity of the monolayer. Conductive STM and AFM probes can serve as top electrodes and form temporary junctions to characterize the charge transport properties of a single molecule or a few molecules from a self-assembled monolayer, but their applications towards practical electronic devices are limited. At present, there are mainly three universal strategies for fabricating large-area junctions comprising SAMs: i) directly forming metallic electrodes via thermal/electron beam evaporation in vacuum or electrochemical deposition; ii) utilizing conductive polymers or nanomaterials as top electrodes; iii) employing liquid metals as top electrodes. These techniques will be surveyed in detail in the following sections, in which the first section focuses on state-of-the-art techniques including lift-and-float approach, nanopore and nanowell, on-wire lithography, crossbars and crosswires, self-aligned lithography, on-edge molecular junctions, and the second section solely focuses on eutectic Ga-In (EGaIn) electrodes because it is extensively employed and innovated in the following thesis chapters (**Chapters 2-6**).

1.3.1. JUNCTIONS USING SOLID ELECTRODES

Lift-and-float approach By floating conductive/semiconductive films onto target substrates, the lift-and-float approach aims to mitigate the damage to the SAMs during the deposition of top electrodes, *e.g.*, by thermal evaporation in vacuum. The immobilization of the top electrodes exploits the capillary interactions between the solid (the conductive/semiconductive film and the target substrate) and the liquid used to float the top electrodes. The technique is often called the lift-off float-on (LOFO) approach which originated from the deposition of GaAs films onto substrates as part of the sample preparation in transmission electron microscopy[129] and was later developed for molecular electronics[130] (Fig. 1.2). The general procedure of the LOFO approach can be described in four steps: i) the fabrication of the conductive/semiconductive film as top electrode onto a solid support, for example, a glass slide; ii) the detachment and flotation of the film onto a liquid surface; iii) the fabrication of SAMs onto the target substrate; iv) the transfer of the floated film onto the as-prepared target substrate to fabricate a junction.

The LOFO approach is compatible with multiple materials for top electrodes including GaAs, Si, ZnO and metals (Au, Ag and Al)[130, 132–135], but mitigates common issues

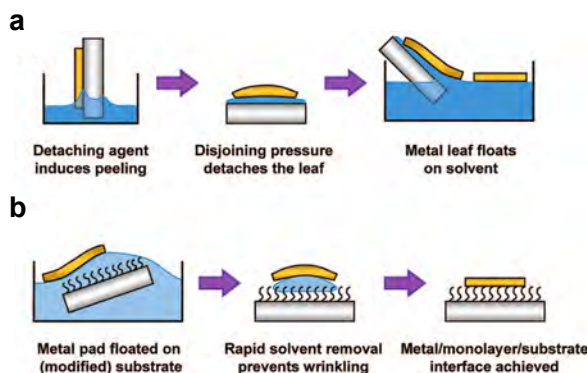


Figure 1.2 | Schematic of the lift-off float-on approach. **a**, lift-off of evaporated leaf from a glass slide using a detaching agent. **b**, float-on of the leaf on the solid substrate in a liquid medium. Reprinted with permission from Ref. [131]. Copyright 2008 American Chemical Society.

such as the generation of pinholes, thermal and mechanical stress as a result of film formation and invasive chemical damage in the fabrication of electrodes using vacuum deposition techniques. By exploiting capillary interactions, the force applied to the SAMs and the fabrication of the top electrode is less invasive. However, the generation of air gaps or wrinkles between the top electrode and the target substrate often results in ill-defined junctions with low reproducibility.

Nanopore and nanowell The nanopore/nanowell approach is used to fabricate molecular junctions comprising SAMs with well-defined junction size at nm^2 scale to reduce grain boundaries and defects that give rise to short circuits. In general, the fabrication of a nanopore device starts with creating a bowl-shaped hole (~ 50 nm in diameter) on a Si_3N_4 membrane using electron beam lithography (EBL) and reactive ion etching (RIE) (Fig. 1.3a).[136] The top electrode (~ 200 nm Au) is thermally evaporated onto the top side of the membrane and fills the pore, followed by the fabrication of SAMs on the electrode in solution and the thermal deposition of the bottom Au electrode onto the SAM to complete the junction. Similarly, patterned Au on a silicon wafer is used as bottom electrode and covered by a layer of SiO_2 in nanowell devices (Fig. 1.3b).[137] The nanowell (~ 10 -40 nm in diameter) is created on the SiO_2 layer using the focused ion beam technique, followed by the growth of SAMs in solution and the deposition of top electrodes.

The sample-to-sample variation in the electrical behaviors of junctions as a result of multi-step fabrication is one of the disadvantages of this approach. Additionally, the yield of the nanopore and nanowell devices (*i.e.*, devices that do not precipitate shorts or fail to conduct) is low ($\sim 2\%$) due to the penetration of metal atoms into the SAMs during deposition that eventually leads to short circuits. To mitigate the damage to the SAMs and increase the yield of the junctions, researchers have developed alternative strategies by inserting a conductive buffer layer, *e.g.*, poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonic acid) (PEDOT:PSS)[138], multilayer graphene[139], Au nanoparticles (AuNPs)[140], single-walled carbon nanotubes (SWNT) networks[141] and carbon paste[142], between the metal electrode and the monolayer. The technique was first demonstrated by fabricating high-yield large-area molecular junctions with conductive

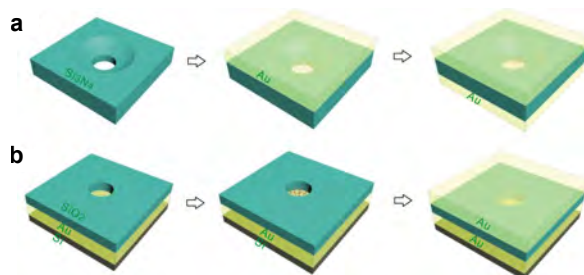


Figure 1.3 | Schematic of large-area junctions based on nanopore and nanowell approaches. **a**, In a nanopore junction, a pore is fabricated through the Si_3N_4 membrane via etching. Au is then evaporated onto the top side of the membrane to obtain the top electrode. A self-assembled monolayer is then grown on the top electrode, followed by the deposition of the opposite electrode to the bottom of the pore. **b**, In a nanowell junction, a hole is drilled through the SiO_2 layer to expose the bottom electrode. After a self-assembled monolayer is grown in the well, a top electrode is fabricated on top of the well. Reprinted with permission from Ref. [48]. Copyright 2016 American Chemical Society.

polymer PEDOT:PSS as the buffer layer between the top electrode and the SAMs. Similar to the original nanopore/nanowell approach, the fabrication starts with the deposition of a bottom electrode and the production of holes using a standard photolithographic technique which allows the growth of SAMs. The key to the buffer-layer approach is the deposition of PEDOT:PSS that serves as a non-invasive top contact on the SAMs, followed by the deposition of an extra Au top electrode and the removal of excess PEDOT:PSS by using RIE. Recent demonstrations that used conductive AuNPs as buffer layer significantly improve the scalability of devices toward practical wafer-scale applications. However, the demonstration of these approaches was not fully extended to SAMs other than saturated alkanethiols hence their compatibility with functional SAMs (*e.g.*, switches and diodes) is yet to be tested.

On-wire lithography The on-wire lithography approach resembles the concept of nanopore/nanowell in combination with template-directed synthesis of nanowires and electrochemical deposition (Fig. 1.5).[143] In a typical molecular junctions developed by on-wire lithography, pillars of multilayered metals are grown electrochemically in a removable template of polycarbonate, in which one of the metal layers serves as a sacrificial layer and defines the junctions width. Then the fabrication continues with the deposition of a silica layer on the pillars to maintain the device structure after the removal of template and sacrificial layers. The crucial step in this procedure is the insertion of molecules into the gap as the length of the molecule, or the size of the composite has to match the width of the junction. Three major approaches were reported to deliver this last step of fabrication: i) "dip-pen" nanolithography, by which molecules such as conductive polymers are deposited into the gap by an AFM tip via capillary transport[144]; ii) self-assembly, by which a self-assembled monolayer is grown in the gap via covalent bonds between the molecules to both electrodes[145]; iii) click chemistry, by which SAMs of shorter molecules are formed on the electrodes to provide reaction sites and the gap is bridged over a step-wise synthesis using click chemistry[146]. Yet this technique is limited to its low throughput in characterizing the charge transport properties and fabrication of the junctions as only one device can be produced at a time.

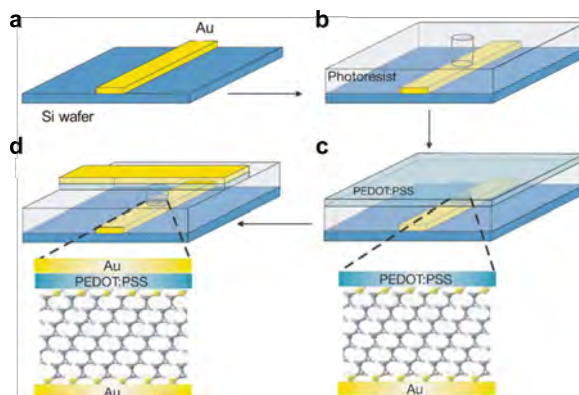


Figure 1.4 | Schematic of the fabrication of nanowell junctions using PEDOT:PSS buffer layer. **a**, The bottom Au electrodes are deposited on a Si wafer. **b**, The photoresist is spincoated onto the wafer, and the holes are photolithographically defined in the photoresist. **c**, A highly conductive polymer PEDOT:PSS is spincoated above the photoresist as top electrode. A self-assembled monolayer is sandwiched between the Au bottom electrode and PEDOT:PSS. **d**, Au electrode is deposited on top of PEDOT:PSS, followed by the removal of redundant polymer using reactive ion etching. Reprinted with permission from Ref. [138]. Copyright 2006 Nature Publishing Group.

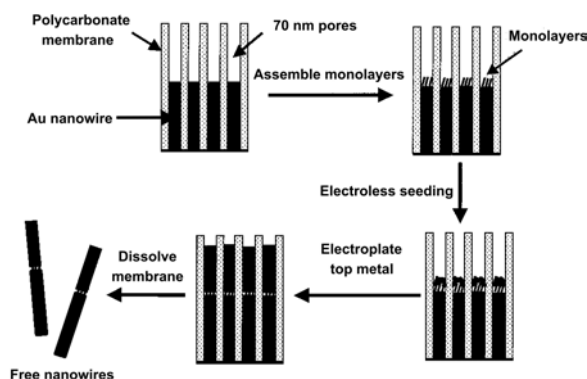


Figure 1.5 | Synthetic scheme for the fabrication of molecular junctions comprising self-assembled monolayers using on-wire lithography. Reprinted with permission from Ref. [143]. Copyright 2002 American Chemical Society.

Transfer printing The transfer printing approach aims to scale up the production of molecular devices in a rapid and simple fashion towards the applications in integrated circuits. Nanotransfer imprinting lithography (NIL) was first introduced as a non-invasive technique to deposit top electrodes for large-area junctions comprising SAMs of alkanethiols (Fig. 1.6).[108] In the demonstrated procedure, a Au-coated polydimethylsiloxane (PDMS) elastomer was brought into contact with the SAMs of 1,8-octanedithiols on GaAs substrates. Because of its stronger interaction with the SAMs over PDMS as a result of covalent bonds, the Au patterns are easily removed from the PDMS stamp and transferred onto the bottom substrate as top electrodes without damaging the SAMs. Other materials such as ultrasmooth Si[147] and block-copolymer self-assemblies[148] were developed to improve the quality and the resolution of the top electrodes respectively. Recently, a technique known as polymer-assisted lift-off (PALO) was introduced as an alternative approach to the rapid fabrication of crossbar junctions comprising SAMs.[134] In this process, a spincoated poly(methyl methacrylate) (PMMA) film is used as a backing layer for the patterned top electrodes which are fabricated on a layer of sacrificial polymer. The removal of the sacrificial layer detaches the electrodes and the PMMA backing layer to float onto water, which then transfer onto the bottom electrodes to form crossbar junctions.

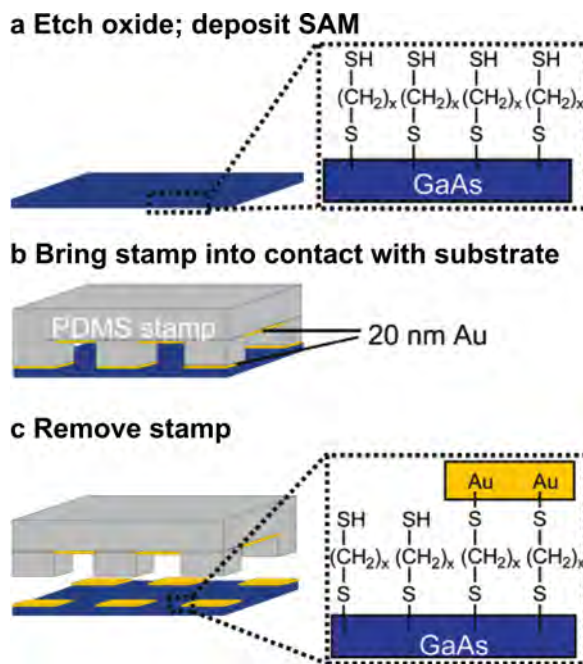


Figure 1.6 | Schematic of the nanotransfer printing procedure. **a**, The GaAs substrate is first etched in concentrated NH_4OH or HCl for 2 min and then immediately exposed to 1,8-octanedithiol vapor or solution for 15 min. **b**, Au-coated elastomeric PDMS stamp with appropriate relief features is brought into contact with the treated substrate. **c**, Removal of the stamp from the substrate completes the printing process. Au on the raised part of the PDMS stamp is bonded and transferred to the dithiol-coated GaAs. Reprinted with permission from Ref. [108]. Copyright 2003 American Chemical Society.

Self-aligned lithography The self-aligned lithography method is considered as an alternative approach to the aforementioned on-wire lithography towards the fabrication of integrated molecular junctions in large quantity (Fig. 1.7.[149]) In the procedure, the first Pt electrode is fabricated with a layer of Al on top using electron beam lithography (EBL), followed by the deposition a second Pt electrode. Unlike on-wire lithography in which the size of the junction is defined by the sacrificial layers, the distance between the two electrodes in self-aligned lithography are defined by the thickness of the Al_2O_3 overhang which subsequently grows onto the Al upon exposure to ambient oxygen and is removed afterwards, providing the alignment between the electrodes. In combination with click-chemistry using bifunctional molecules that selectively binds to single electrode, this method mitigates the problem of non-selective binding in the on-wire lithography technique and offers the diversity over materials that can be implemented into the molecular junctions. A dielectric layer can be easily added into the top electrode and bottom conductive substrate, which can be used to study the charge transport properties of the molecular ensembles gated by an external electric field.

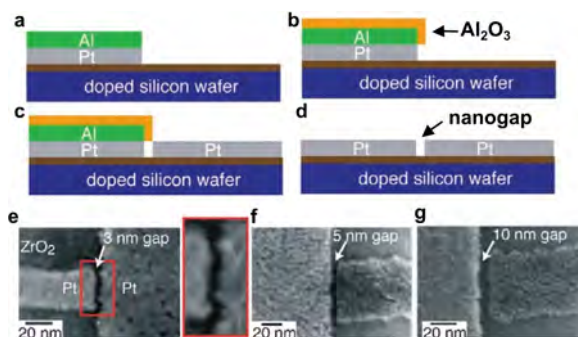


Figure 1.7 | Schematic and characterization of the fabrication of nanoscale electrodes based on self-aligned lithography. **a**, A line of Al on Pt is patterned by electron-beam lithography on a silicon wafer coated with ZrO_2 . **b**, Oxygen in the ambient oxidizes Al to produce an overhanging Al_2O_3 layer. **c**, Evaporation of the counter electrode produces Pt separated by the amount of Al_2O_3 overhang. **d**, Dissolving the Al/ Al_2O_3 layer gives closely spaced Pt electrodes. **e-g**, Scanning electron micrograph showing a 3-nm (**e**), 5-nm (**f**) and 10-nm (**g**) gap; the part in the highlight region is enlarged by 200 % on the right. Reprinted with permission from Ref. [149]. Copyright 2007 Wiley-VCH.

On-edge molecular junction On-edge molecular junctions are constructed vertically in which the electrodes are separated by an insulating layer and molecules are covalently bound to the exposed edges of the electrodes upon chemical etching of the insulating layer[150]. Unlike the aforementioned techniques in which the sacrificial layers between the electrodes are eventually removed, the insulating layer in the on-edge molecular junction remains intact throughout the device fabrication, and as a result, two tunneling junctions (one formed by the insulating layer and the other by the molecules) function simultaneously in one device. One of the challenges with this technique is the trade-off between the thickness of the insulating layer and the molecules, for example, a thinner gap between electrodes increases the leakage current exponentially but a larger gap requires the synthesis of longer molecules that poses limitation on studying charge transport properties related to molecular length. While the fabrication procedure is improved

with high quality insulating materials[151] and the junctions are used as testbed for biomolecules such as DNA nucleotides[152], the overly broadened data distribution largely due to the lack of well-defined molecular structure may undermine the practical utilization of this technique in terms of stability and reproducibility.

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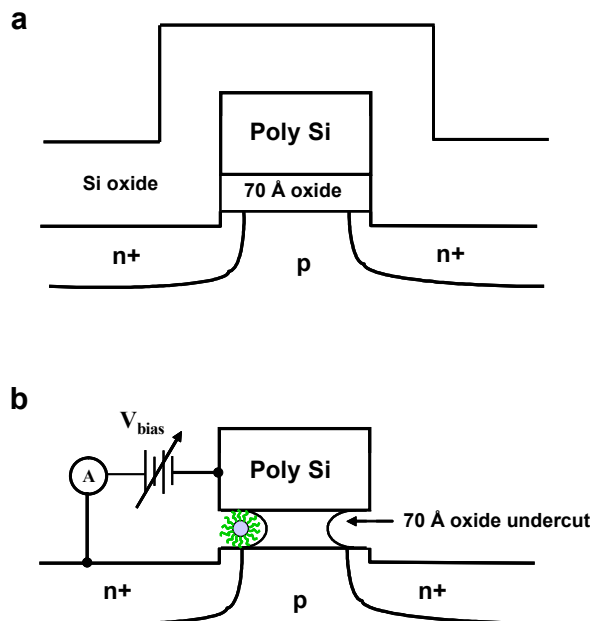


Figure 1.8 | Schematics of the cross-sections of the on-edge molecular junctions. **a**, The structure of the junction before etching of the oxide passivation layer. **b**, The structure of the junctions after partial removal of oxide and the assembly of nanoparticles functionalized by organic molecules. Reprinted with permission from Ref. [150]. Copyright 2005 IOP Publishing Ltd.

1.3.2. JUNCTIONS USING EGaIn ELECTRODES

Eutectic Ga-In, or EGaIn (75.5% Ga and 24.5% In by weight) was introduced to replace Hg as one of the electrodes for large-area junctions.[153] EGaIn is liquid at room temperature (melting point 15.7 °C), however, it does not flow like water (or Hg) due to its shear thinning non-Newtonian behavior. Despite the similar work functions of EGaIn (~4.2 eV) and Hg (~4.5 eV), EGaIn spontaneously grows a thin layer of Ga_2O_3 (~0.5-3 nm thick) in air that confines the movement of EGaIn[154–156], thus allowing the manipulation of EGaIn into various shapes for specific applications. In the experiment, a conical tip is formed easily and reproducibly by raising a syringe over an EGaIn droplet until their separation, which can be directly used as a high-throughput, non-invasive technique for the characterization of charge transport in large-area junctions comprising SAMs (Fig. 1.9). Unlike Hg, the EGaIn tip does not retract to a spherical droplet due to the presence of the limiting Ga_2O_3 layer, which drastically reduces the contact area and therefore increases the yield of large-area junctions. The charge transport in these large-area junctions is

neither dominated by the EGaIn electrode nor the Ga_2O_3 layer but the self-assembled monolayers.[157] Though large-area junctions using EGaIn top electrode may suffer from data variation dependent on the geometry of the tip and the mechanical stability of the junctions[158], such challenges can be mitigated by operating the EGaIn electrode at its optimal condition, such well-controlled back pressure and constant contact area[159].



Figure 1.9 | A series of photographs of the formation of a conical tip of EGaIn. From left to right: a micromanipulator i) brings a drop of EGaIn suspended from the needle of a syringe into contact with the bare, reflective surface of a Ag film, and ii) raises the syringe until the EGaIn separates into a conical tip (which remains attached to the needle of the syringe) and a drop on the Ag surface. The pictures are sequential and show the formation of a single tip; the time spanned by this sequence is less than 5s. Reprinted with permission from Ref. [153]. Copyright 2008 Wiley-VCH.

Besides temporary junctions, the unique rheological and electrical properties of EGaIn enable novel approaches to fabricate electronic devices comprising large-area junctions in combination with unconventional techniques. Cofabrication is such a technique that simplifies the fabrication of multicomponent microelectronic devices by generating correctly aligned features over a single lithographic step, avoiding registration as compared to other commonly-used techniques. The highly efficient fabrication of arrays of large-area tunneling junctions is demonstrated using EGaIn electrodes stabilized in cofabricated microfluidic channels, which does not require cleanroom environment, vacuum deposition or toxic substances.[160] The fabrication of EGaIn electrodes was further improved by stabilizing the liquid metal in micro-sized pore to eliminate edge effect that leads to short circuits and to generate functions as electronic components, *e.g.*, logic gates.[158, 161] Additionally, EGaIn junctions is an effective test bed for investigating the role of binding groups[37], environmental effects[162], substrate roughness[163], molecule-electrode coupling[164] and bond topology[165] in charge transport across large-area junctions. All these aforementioned features combined makes the main driving force to fabricate, study and utilize EGaIn large-area junctions in the research presented in the following chapters (**Chapter 2-6**) of this thesis.

1.4. CHARGE TRANSPORT MECHANISMS

There are two general charge transport mechanisms in molecular junctions based on whether thermal activation is present: i) temperature-independent direct tunneling or Fowler-Nordheim tunneling, and ii) temperature-dependent hopping conductance or thermionic emission.[166–168] And because of their distinct differences in the relationships between current density, electrostatic barrier dimensions, voltage and temperature, electrical measurements that investigate the charge transport properties with variable molecular length or temperature provide useful information to identify the transport

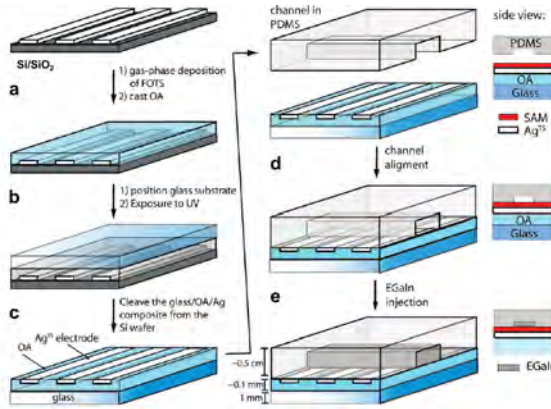


Figure 1.10 | Fabrication of the arrays of SAM-based tunneling junctions. **a**, The pattern of Ag electrodes are fabricated using photolithography, electron-beam deposition of Ag and lift-off. **b**, A glass substrate is affixed to the pattern of the Ag electrodes using a UV-curable adhesive. The cured optical adhesive interacts strongly with the Ag and the glass support but not with the wafer. **c**, The Ag/adhesive/glass composite is cleaved from the wafer by applying a razor blade with gentle pressure in a direction parallel to the wafer, between the glass substrate and the wafer. **d**, A microchannel in PDMS is aligned perpendicular to the electrodes after forming the SAMs on these electrodes. **e**, The microchannels are then filled with EGaIn to complete the device. Reprinted with permission from Ref. [160]. Copyright 2010 American Chemical Society.

mechanism of a molecular junction. In non-resonant tunneling, the energies of the injected electrons do not precisely match the energies of the molecular orbitals and the electrons traverse the junctions in a single step without taking temporary residence on the molecules. The current density of the junctions then decreases exponentially with increasing molecular length by following

$$J = J_0 \exp(-\beta d) \quad (1.1)$$

where J_0 is the injection current density (*i.e.*, the current flowing through an ideal junction in the absence of a tunneling barrier), d is the molecular length and β is a tunneling decay coefficient determined by the height of the effective tunneling barrier which is often approximated at low-bias regime as the difference between the Fermi levels of the electrodes (E_f) and the frontier states (lowest unoccupied states and highest occupied states) of the molecules.[167]

In hopping charge transport, electrons are injected into the frontier states of the molecules and incoherently (*i.e.*, the consistency of the frequency and the waveform of the electrons is lost) hop between several discrete states before being captured by an electrode. Despite their coexistence in molecular junctions, the tunneling process is suppressed in junctions comprising long conjugated molecules, *e.g.*, oligothiophenes with more than 11 repeating units, in favor of the thermally activated hopping process.[169, 170] The relationship between the current density of the junction and the temperature is expressed as the following

$$J = J_0 \exp(-E_a/kT) \quad (1.2)$$

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where J_0 is the injection current density of the junction, E_a is the activation energy defined by the energy required to reach the transition state for electron transfer within the molecule. The combination of Eq. 1.1 and Eq. 1.2 provides a fundamental standard for the identification of charge transport mechanism in molecular junctions: if the current density decreases exponentially with increasing molecular length, but remains relatively constant under variable temperatures, the mechanism is likely non-resonant tunneling; if the current density gradually decreases as the junction cools down, thermally assisted hopping is likely involved.

A charge transport process that incorporates both tunneling and hopping mechanisms can give rise to useful electrical phenomena, *e.g.*, rectification. For example, large-area junctions comprising SAMs of ferrocenyl alkanethiols facilitate asymmetric charge transport with large rectification ratio.[160] Variable temperature measurements confirm hopping and tunneling as the dominant mechanisms at cathodic (negative) and anodic (positive) potentials, respectively. The redox-active ferrocene moiety plays a crucial role in the generation of rectification, which has the highest occupied molecular orbitals (E_{HOMO}) close to the E_f of the top electrode to facilitate the hopping of injected electrons. Asymmetric charge transport was also observed in large-area junctions comprising fullerene-terminated SAMs, in which the lowest unoccupied π states of the fullerene moieties come into resonance with the top electrode.[104, 128]

Non-resonant tunneling and thermally assisted hopping are not the only charge transport mechanisms in molecular junctions, *e.g.*, Fowler-Nordheim tunneling was found in the charge transport across 20 nm-long molecular wire at high bias[22] and thermal emission of electrons was found in the rectifying SAMs of 4-thioacetylphenyl[166]. However, these mechanisms can be effectively distinguished by thoroughly examining the molecular length/temperature/voltage dependence of current density, which is demonstrated in numerous reports and **Chapter 4-5** as a well-established method.

1.5. OUTLINE OF THESIS

The thesis aims to unite the synthesis and characterization of novel (bio)organic semiconductive materials and the fabrication of electronic devices for paradigm-shifting applications. In **Chapter 2**, we examined the relationship between mechanical deformation and the electronic properties of SAMs of oligothiophenes in tunneling junctions using conductive probe AFM and EGaIn. We compared shifts in conductivity and transition voltages with increasing AFM tip force load to SAMs of alkanethiolates. While these shifts result from an increasing tilt angle from penetration of the SAM by the AFM tip for the latter, we ascribe them to distortions of the π system present in oligothiophenes, which is more mechanically robust than alkanethiolates of comparable length; SAMs comprising oligothiophenes show about five times higher Young's modulus (a measure of the stiffness of a solid material in elastic regime) than alkanethiolates. The mechanical robustness of oligothiophenes manifests as an increased tolerance to high bias in large-area EGaIn junctions suggesting that electrostatic pressure plays a significant role in the short circuit of molecular junctions at high bias.

In **Chapter 3**, we described a strategy for the fabrication of soft, stretchable biophotovoltaic devices that generate photocurrent from light-harvesting photosystem I (PSI)

complexes that are self-assembled onto Au electrodes with a preferred orientation. Charge is collected by the direct injection of electrons into the Au electrode and the transport of holes through a redox couple to EGaIn electrodes that are confined to microfluidic pseudochannels by arrays of posts. The pseudochannels are defined in a single fabrication step that exploits the non-Newtonian rheology of EGaIn. This strategy is extended to the fabrication of reticulated electrodes that are inherently stretchable. A simple shadow evaporation technique is used to increase the surface area of the Au electrode by a factor of 10^6 compared to planar electrodes. The power conversion efficiency of the biophotovoltaic devices decrease over time, presumably as the PSI complexes denature and/or detach from the Au electrodes. However, by circulating a solution of active PSI complexes the devices self-regenerate by mass action/self-assembly. These devices leverage simple fabrication techniques to produce complex function and prove that photovoltaic devices comprising PSI can retain the ability to regenerate, one of the most important functions of photosynthetic organisms.

The relatively simple and versatile chemistry of metal-thiolate bonds makes SAMs of thiolates the preferred option for engineering the surface properties of metals toward a range of applications, yet fragility and a tendency to oxidize in air limit their long-term use. In **Chapter 4**, we reported the formation of thiol-free self-assembled mono- and bilayers of glycol ethers, which bind to the surface of coinage metals through the spontaneous chemisorption of glycol ether-functionalized fullerenes. As-prepared assemblies are bilayers presenting fullerene cages at both the substrate and ambient interface. Subsequent exposure to functionalized glycol ethers displaces the topmost layer of glycol ether-functionalized fullerenes, and the resulting assemblies expose functional groups to the ambient interface. These layers exhibit the key properties of thiolate SAMs, yet they are stable to ambient conditions for several weeks, as shown by the performance of tunneling junctions formed from SAMs of alkyl-functionalized glycol ethers. Glycol ether-functionalized spiropyran incorporated into mixed monolayers lead to reversible, light-driven conductance switching. Self-assemblies of glycol ethers are drop-in replacements for thiolates SAMs that retain all of their useful properties while avoiding the drawbacks of metal-thiolate bonds.

In the following **Chapter 5**, we describe the reconfiguration of molecular tunneling junctions during operation via the self-assembly of bilayers of glycol ethers. We use well-established functional groups to modulate the magnitude and direction of rectification in assembled tunneling junctions by exposing them to solutions containing different glycol ethers. Variable-temperature measurements establish that rectification occurs by a bias-dependent tunneling-hopping mechanism and that glycol ethers, beside being an unusually efficient tunneling medium, behave identically to alkanes. We fabricated memory bits from crossbar junctions prepared by injecting EGaIn into microfluidic channels. Two 8-bit registers were able to perform logical AND operations on bit strings encoded into chemical packets as microfluidic droplets that alter the composition of the crossbar junctions through self-assembly to effect memristor-like properties. This proof of concept work demonstrates the potential for fieldable molecular-electronic devices based on tunneling junctions of self-assembled monolayers and bilayers.

In **Chapter 6**, we successfully fabricated the SAMs of magnetic phthalocyaninato lanthanide-ligated polyoxovanadate cages on atomically smooth Au substrates. These

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SAMs exhibit varied conductance in large-area molecular junctions using EGaIn top electrodes at low bias but similar conductance at high bias, which corresponds to the molecular states coming into resonance with the electrode/substrate E_f at higher voltage. While the magnetism of these metal complexes are dominated by the spin-orbit effects of lanthanide cations, the molecular charge-transport characteristics are strongly influenced by electron transport through the fully-oxidized vanadium center.

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